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(54) Process for the preparation of hydrocarbon fuels

Verfahren zur Herstellung von Kohlenwasserstoffbrennstoffen

Procédé de préparation de combustibles hydrocarbonés

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(56) References cited:

EP-A- 0 127 220	EP-A- 0 147 873
EP-A- 0 321 303	EP-A- 0 370 757
EP-A- 0 515 270	EP-A- 0 635 557
GB-A- 2 077 289	US-A- 4 080 397
US-A- 4 423 265	US-A- 4 943 672

- "Engineering Aspects of the Conversion of Natural Gas Into Middle Distillates" M.M.G. Sonden et al., NATOASI I, Ser. 275,, 227-247 (1992)
- "Shell Middle Distillate Synthesis Process", M.M., J.van der Burgt et al., 5th Synfuels Worldwide Symposium (1985)

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Description

[0001] The present invention relates to a process for the preparation of gasoil, in particular to a process for the preparation of gasoil from a mixture of carbon monoxide and hydrogen.

[0002] The preparation of hydrocarbons from a mixture comprising carbon monoxide and hydrogen by contacting the mixture with a suitable synthesis catalyst at elevated temperatures and pressures is known in the art as the Fischer-Tropsch synthesis. It is known in the art to apply Fischer-Tropsch synthesis processes in the preparation of a range of principally aliphatic hydrocarbons having a wide range of molecular weights. Of particular interest, however, is the use of the Fischer-Tropsch synthesis to prepare hydrocarbons suitable for use as fuels, for example hydrocarbons having boiling points within the boiling point ranges of naphtha and the middle distillates.

[0003] For the purposes of this specification, the term "middle distillates" as used herein is to be taken as a reference to hydrocarbons or hydrocarbon mixtures having a boiling point or boiling point range substantially corresponding to that of the kerosine and gasoil fractions obtained during the conventional atmospheric distillation of crude oil. The term "naphtha" as used herein is a reference to hydrocarbons or hydrocarbon mixtures having a boiling point or boiling point range substantially corresponding to that of the naphtha (sometimes referred to as the gasoline) fractions obtained during the conventional atmospheric distillation of crude oil. In such a distillation, the following fractions are consecutively recovered from the crude oil: one or more naphtha fractions boiling in the range of from 30 to 220 °C, one or more kerosine fractions boiling in the range of from 120 to 300 °C and one or more gasoil fractions boiling in the range of from 170 to 370°C. The term "hydrocarbon fuel" is to be taken as a reference to either one of or a mixture of naphtha and middle distillates.

[0004] In order to improve the yield of valuable hydrocarbon fuel products from the Fischer-Tropsch synthesis process, a variety of process schemes have been proposed for upgrading the Fischer-Tropsch products. Thus, in US patent No.4,125,566(US-A-4,125,566) a process scheme is disclosed in which the highly olefinic effluent of a Fischer-Tropsch synthesis is treated by one or more of distillation, polymerisation, alkylation, hydrotreatment, cracking-decarboxylation, isomerisation and hydrotreatment. The process scheme of US-A-4,125,566 yields products lying mainly in the gasoline, kerosene and gasoil ranges.

[0005] From the variety of aforementioned processes which may be applied in upgrading the products of a Fischer-Tropsch synthesis, a number of process schemes have been proposed which rely upon the application of hydrotreatment processes in the upgrading. Thus, US patent No. 4,478,955 (US-A-4,478,955) discloses a process scheme comprising contacting the effluent of a Fischer-Tropsch synthesis process with hydrogen in the presence of a suitable hydrogenation catalyst. The effluent of the Fischer-Tropsch synthesis is described in US-A-4,478,955 as comprising predominantly olefins and carboxylic acids. Under the action of the hydrogenation treatment, useful fuel components comprising alkanes, alcohols and esters are produced.

[0006] In an alternative process scheme disclosed in US patents Nos. 4,059,648 and 4,080,397 (US-A-4,059,648 and 4,080,648), the products of a Fischer-Tropsch synthesis are upgraded by being subjected firstly to a hydrotreatment and thereafter fractionated. Selected fractions of the fractionated product are subsequently subjected to a selective hydrocracking process in which the fractions are contacted with a special zeolite catalyst capable of transforming the aliphatic hydrocarbons present in the fractions into aromatic hydrocarbons. The resulting aromatic-rich product is said to be useful as gasoline and light and heavy fuel oils.

[0007] More recently, much interest has been paid to the application of the Fischer-Tropsch synthesis in the preparation of substantially paraffinic hydrocarbon products suitable for use as fuels. Whilst it is possible to use the Fischer-Tropsch synthesis process to directly prepare paraffinic hydrocarbons having boiling points in the boiling point ranges of the valuable fuel fractions, it has been found most advantageous to use the Fischer-Tropsch synthesis process to prepare high molecular weight paraffinic hydrocarbons having a boiling point above the upper limit of the boiling point range of the middle distillates and subject the products so-obtained to a selective hydrocracking process to yield the desired hydrocarbon fuels.

[0008] Thus, in United Kingdom patent No. 2 077 289 (GB 2077289 B), a process is disclosed comprising contacting a mixture of carbon monoxide and hydrogen with a catalyst active in the Fischer-Tropsch synthesis and thereafter cracking the resulting paraffinic hydrocarbons in the presence of hydrogen to yield middle distillates. A similar process scheme is disclosed in European patent application publication No. 0 147 873 (EP-A-0 147 873).

[0009] Most surprisingly, it has been found advantageous if the products of a Fischer-Tropsch synthesis yielding substantially paraffinic hydrocarbons are first subjected to a mild hydrogenation, under conditions such that substantially no isomerisation or hydrocracking of the hydrocarbon occurs, and thereafter are subjected to a selective hydrocracking treatment to yield desired gasoil.

[0010] Accordingly, the present invention provides a process for the preparation of gasoil comprising the steps of:

- a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic hydrocarbon product, containing at least 70 %wt par-

affins;

b) contacting the hydrocarbon product so-obtained with hydrogen in the presence of a hydroconversion catalyst under conditions such that the conversion, defined as the percent weight of the fraction of the hydrocarbon product feed boiling above 370 °C which is converted during the hydroconversion to a fraction boiling below 370 °C, is below 20%; separating the C₄- fraction from the higher molecular weight fraction and

c) contacting at least part of the higher molecular weight hydrocarbon product of step (b) with hydrogen in the presence of a hydroconversion catalyst not containing any crystalline zeolite under conditions such that hydrocracking and isomerisation of the product occurs to yield a substantially paraffinic hydrocarbon fuel, containing at least 95 %wt paraffins, and isolating the gasoil from the hydrocarbon fuel, the conversion being at least 40 %.

[0011] In the two-stage processes disclosed in the prior art, in particular GB 2077289 B and EP-B-0 147 873, the products of the hydrocarbon synthesis stage are subjected to a hydroconversion treatment. The primary objective of the hydro-conversion is to convert, by hydrocracking, the high molecular weight, paraffinic products of the synthesis stage into the desired hydrocarbon fuels, for example middle distillates. However, a number of additional reactions occur together with the hydrocracking reactions during the hydroconversion. In particular, the hydroconversion treatment serves to isomerise a portion of the linear paraffinic hydrocarbons, which in turn improves the properties of the hydrocarbon fuels. In addition, the action of the hydroconversion treatment is to hydrogenate the minor quantities of olefinic and oxygen-containing compounds formed during the hydrocarbon synthesis reactions and which are undesirable components in hydrocarbon fuels.

[0012] In contrast to the processes of the prior art, the hydrocarbons prepared in the first stage, stage (a), of the process of the present invention are subjected to a hydroconversion in two separate and distinct stages. In the first hydroconversion stage, stage (b), the olefinic and oxygen-containing compounds are hydrogenated, followed by removal of the C₄- fraction from the higher molecular weight fraction. However, as an essential feature of this process, the operating conditions of the first hydroconversion stage are selected so as to substantially prevent hydrocracking and/or hydroisomerisation reactions from occurring.

[0013] In the second hydroconversion stage of the process of the present invention, stage (c), the desired hydrocarbon fuels are prepared by subjecting at least a part of the higher molecular weight product of the first hydroconversion stage to a second hydroconversion treatment, in which the high molecular weight paraffinic hydrocarbons are hydroisomerised and hydrocracked using a catalyst not containing any crystalline zeolite. Most surprisingly, it has been found that a number of major advantages result from the application of a two-stage hydroconversion regime of the present invention, compared with the single-stage hydroconversion of the prior art.

[0014] Firstly, water is formed as a product of the hydrogenation of the oxygen-containing hydrocarbons. It has been found that water produced during this reaction adversely affects certain hydroconversion catalysts, leading to a reduction in catalyst performance. Secondly, it has been found that milder operating conditions are required in the second hydroconversion stage to achieve the desired degree of hydrocracking and hydroisomerisation than required in the single hydroconversion stage of the prior art process. This results in an improved lifetime of the hydroconversion catalyst and, most surprisingly, leads to a markedly improved product. In addition, the process of the present invention most surprisingly exhibits an improved selectivity to gasoil, compared with the processes of the prior art.

[0015] For the purposes of this specification, the term "substantially paraffinic" when used in connection with hydrocarbon products refers to a hydrocarbon mixture comprising at least 70 %wt paraffins, preferably at least 80 %wt paraffins. Gasoil produced by the process of this invention comprises at least 95 %wt paraffins.

[0016] In step (a) of the process of the present invention, a feed comprising a mixture of carbon monoxide and hydrogen is contacted at elevated temperature and pressure with a catalyst active in the synthesis of paraffinic hydrocarbons. Suitable processes for the preparation of the mixture of carbon monoxide and hydrogen are well known in the art and include such processes as the partial oxidation of methane, typically in the form of natural gas, and the steam reforming of methane. The relative amounts of carbon monoxide and hydrogen present in the feed may vary over a wide range and may be selected according to the precise catalyst and process operating conditions being employed. Typically, the feed contacting the catalyst comprises carbon monoxide and hydrogen in a hydrogen/carbon monoxide molar ratio of below 2.5, preferably below 1.75. More preferably, the hydrogen/carbon monoxide ratio is in the range of from 0.4 to 1.5, especially from 0.9 to 1.3. Unconverted carbon monoxide and hydrogen may be separated from the synthesis product and recycled to the inlet of the synthesis reactor.

[0017] Suitable catalysts for use in the synthesis of paraffinic hydrocarbons are known in the art. Typically, the catalyst comprises, as the catalytically active component, a metal from Group VIII of the Periodic Table of Elements. Particular catalytically active metals from Group VIII include ruthenium, iron, cobalt and nickel. For the process of the present invention, a catalyst comprising cobalt as the catalytically active metal is preferred.

[0018] The catalytically active metal is preferably supported on a porous carrier. The porous carrier may be selected from any suitable refractory metal oxide or silicate or mixture thereof. Particular examples of preferred carriers include silica, alumina, titania, zirconia and mixtures thereof. Carriers comprising silica and/or alumina are especially preferred.

[0019] The catalytically active metal may be applied to the carrier by any of the techniques known in the art, for example comulling, impregnation or precipitation. Impregnation is a particularly preferred technique, in which the carrier is contacted with a compound of the catalytically active metal in the presence of a liquid, most conveniently in the form of a solution of the metal compound. The compound of the active metal may be inorganic or organic, with inorganic compounds being preferred, in particular nitrates. The liquid employed may also be either organic or inorganic. Water is a most convenient liquid.

[0020] The amount of catalytically active metal present on the carrier is typically in the range of from 1 to 100 parts by weight, preferably 10 to 50 parts by weight, per 100 parts by weight of carrier material.

[0021] The catalytically active metal may be present in the catalyst together with one or more metal promoters or cocatalysts. The promoters may be present as metals or as the metal oxide, depending upon the particular promoter concerned. Suitable metal oxide promoters include oxides of metals from Groups IIA, IIIB, IVB, VB or VIB of the Periodic Table, oxides of the lanthanides and/or the actinides. Preferably, the catalyst comprises an oxide of an element in Group IVB of the Periodic Table, in particular titanium or zirconium. Catalysts comprising zirconium are especially preferred. As an alternative or in addition to the metal oxide promoter, the catalyst may comprise a metal promoter selected from Groups VIIB and/or VIII of the Periodic Table. Preferred metal promoters include platinum and palladium. A most suitable catalyst comprises cobalt as the catalytically active metal and zirconium as a promoter. The promoter may be incorporated in the catalyst using any of the methods discussed hereinbefore with respect to the catalytically active component.

[0022] The promoter, if present in the catalyst, is typically present in an amount of from 1 to 60 parts by weight, preferably from 2 to 40 parts by weight, per 100 parts by weight of carrier material.

[0023] The hydrocarbon synthesis is conducted under conditions of elevated temperature and pressure. Typically, the synthesis is effected at a temperature in the range of from 125 to 300 °C, preferably from 175 to 250 °C. The reaction pressure is typically in the range of from 5 to 100 bar, preferably from 12 to 50 bar. The synthesis may be conducted using a variety of reactor types and reaction regimes, for example in a fixed bed regime, a slurry phase regime or an ebullating bed regime.

[0024] The hydrocarbon product of the synthesis stage is subjected to a two-stage hydroconversion treatment in stages (b) and (c) of the process of the present invention. The entire effluent of the synthesis stage may be led directly to the first hydroconversion stage. However, it is preferred to separate from the hydrocarbon product of the synthesis stage the unconverted carbon monoxide and hydrogen and water formed during the synthesis. If desired, the low molecular weight products of the synthesis stage, in particular the C₄- fraction, for example methane, ethane and propane, may also be removed prior to the hydroconversion treatment. The separation is conveniently effected using distillation techniques well known in the art.

[0025] In the first hydroconversion stage, stage (b), the hydrocarbon product is contacted with hydrogen in the presence of a hydrogenation catalyst. Suitable catalysts for use in this stage are known in the art. Typically, the catalyst comprises as catalytically active component one or more metals selected from Groups VIB and VIII of the Periodic Table of Elements, in particular one or more metals selected from molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum and palladium. Preferably, the catalyst comprises one or more metals selected from nickel, platinum and palladium as the catalytically active component.

[0026] A particularly suitable catalyst comprises nickel as a catalytically active component.

[0027] Catalysts for use in the first hydroconversion stage typically comprise a refractory metal oxide or silicate as a carrier. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, alumina and silica-alumina.

[0028] The catalyst may comprise the catalytically active component in an amount of from 0.05 to 80 parts by weight, preferably from 0.1 to 70 parts by weight, per 100 parts by weight of carrier material. The amount of catalytically active metal present in the catalyst will vary according to the specific metal concerned. One particularly suitable catalyst for use in the first hydroconversion stage comprises nickel in an amount in the range of from 30 to 70 parts by weight per 100 parts by weight of carrier material. A second particularly suitable catalyst comprises platinum in an amount in the range of from 0.05 to 2.0 parts by weight per 100 parts by weight of carrier material.

[0029] Suitable catalysts for use in the first hydroconversion stage of the process of this invention are available commercially, or may be prepared by methods well known in the art, for example the methods discussed hereinbefore with reference to the preparation of the hydrocarbon synthesis catalyst.

[0030] In the first hydroconversion stage, the hydrocarbon product is contacted with hydrogen at elevated temperature and pressure. The operating temperature may typically range from 100 to 300 °C, more preferably from 150 to 275 °C, in particular from 175 to 250 °C. Typically, the operating pressure ranges from 5 to 150 bars, preferably from 10 to 50 bars. Hydrogen may be supplied to the hydroconversion stage at a gas hourly space velocity in the range of from 100 to 10000 NI/hr, more preferably from 250 to 5000 NI/hr. The hydrocarbon product being treated is typically supplied to the hydroconversion stage at a weight hourly space velocity in the range of from 0.1 to 5 kg/hr, more

preferably from 0.25 to 2.5 kg/l/hr. The ratio of hydrogen to hydrocarbon product may range from 100 to 5000 NI/kg and is preferably from 250 to 3000 NI/kg.

[0031] The first hydroconversion stage is operated under conditions such that substantially no isomerisation or hydrocracking of the feed occurs. The precise operating conditions required to achieve the desired degree of hydrogenation without substantial hydrocracking or hydroisomerisation occurring will vary according to the composition of the hydrocarbon product being fed to the hydroconversion stage and the particular catalyst being employed. As a measure of the severity of the conditions prevailing in the first hydroconversion stage and, hence, the degree of hydrocracking and isomerisation occurring, the degree of conversion of the feed hydrocarbon may be determined. In this respect, conversion, in percent, is defined as the percent weight of the fraction of the feed boiling above 370 °C which is converted during the hydroconversion to a fraction boiling below 370 °C. The conversion of the first hydroconversion stage is below 20%, preferably below 10%, more preferably below 5%.

[0032] In the process of the present invention, the hydrocarbon product leaving the first hydroconversion stage substantially consists of high molecular weight, paraffinic hydrocarbons having a boiling point range above that of the middle distillates. At least a part of this hydrocarbon product is subjected to a second hydroconversion in stage (c) of the process of this invention, to yield the desired hydrocarbon fuel product. The C₄-fraction is separated from the higher molecular weight hydrocarbons prior to the second hydroconversion stage. The separation may be conveniently achieved using distillation techniques well known in the art. At least a part of the remaining C₅+ fraction of the hydrocarbon product is then used as feed for the second hydroconversion stage.

[0033] In the second hydroconversion stage, hydrocarbon fuels are prepared from the hydrocarbon product of the first hydroconversion stage by hydrocracking and hydroisomerising the product with hydrogen in the presence of a suitable catalyst. Typically, the catalyst comprises as catalytically active component one or more metals selected from Groups VIB and VIII of the Periodic Table of Elements, in particular one or more metals selected from molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum and palladium. Preferably, the catalyst comprises one or more metals selected from nickel, platinum and palladium as the catalytically active component. Catalysts comprising platinum as the catalytically active component have been found to be particularly suitable for use in the second hydroconversion stage.

[0034] Catalysts for use in the second hydroconversion stage typically comprise a refractory metal oxide or silicate as a carrier. The carrier material may be amorphous or crystalline. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, alumina and silica-alumina. A particularly preferred catalyst comprises platinum supported on a silica-alumina carrier.

[0035] The catalyst may comprise the catalytically active component in an amount of from 0.05 to 80 parts by weight, preferably from 0.1 to 70 parts by weight, per 100 parts by weight of carrier material. The amount of catalytically active metal present in the catalyst will vary according to the specific metal concerned. A particularly preferred catalyst for use in the second hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material.

[0036] Suitable catalysts for use in the second hydroconversion stage of the process of this invention are available commercially, or may be prepared by methods well known in the art, for example the methods discussed hereinbefore with reference to the preparation of the hydrocarbon synthesis catalyst.

[0037] In the second hydroconversion stage of this process, the hydrocarbon product of the first hydroconversion stage is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. Typically, the temperatures necessary to yield the hydrocarbon fuels will lie in the range of from 175 to 400 °C, preferably from 250 to 375 °C. The pressure typically applied ranges from 10 to 250 bars, more preferably from 25 to 250 bars. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 NI/l/hr, preferably from 500 to 5000 NI/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably from 0.25 to 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 NI/kg and is preferably from 250 to 2500 NI/kg.

[0038] As discussed hereinbefore in connection with the first hydroconversion stage, the degree of hydrocracking and isomerisation occurring in the second hydroconversion stage may be measured by determining the degree of conversion of the fraction boiling above 370 °C, as hereinbefore defined. The second hydroconversion stage is operated at a conversion of at least 40%.

[0039] The hydrogen required for the operation of both the first and the second hydroconversion stages may be generated by processes well known in the art, for example by the steam reforming of a refinery fuel gas.

[0040] The hydrocarbon fuel produced in the second hydroconversion stage will typically comprise hydrocarbons having boiling points lying in a number of different fuel fractions, for example the naphtha, kerosine and gasoil fractions discussed hereinbefore. Separation of the hydrocarbon fuel into the appropriate fractions may be conveniently achieved using distillation techniques well known in the art.

[0041] The process of the present invention is further described in the following illustrative examples, of which Ex-

amples 1 and 4 are directed to a process according to the present invention and Examples 2, 3 and 5 are for comparison purposes only.

EXAMPLE 1

(A) HYDROCARBON SYNTHESIS STAGE

(i) Catalyst Preparation

[0042] A mixture comprising silica (precipitated silica, average particle size 50 μm , surface area 450 m^2/g), ammonium zirconium carbonate ("Bacote" 20, 20 %wt equivalent of ZrO_2) and water was mulled for a period of about 20 minutes. Acetic acid (5% aqueous solution) and water were added and the mixture mulled for a further period of about 30 minutes. Polyelectrolyte ("Nalco": as a 4% aqueous solution) was added and the resulting mixture mulled for a further 5 minutes to yield a final mixture having a pH of about 8.4 and a loss on ignition of about 70%.

[0043] The resulting mixture was extruded using a 2.54 cm (1 inch) "Bonnot" extruder having a 1.7 mm "Delrin" trilobe dieplate insert to yield trilobe extrudates. The extrudates were dried at a temperature of about 120 $^{\circ}\text{C}$ and finally calcined at a temperature between 500 and 550 $^{\circ}\text{C}$ for 2 hours.

[0044] The calcined extrudates were washed using an aqueous solution of ammonium acetate and thereafter calcined as hereinbefore described. An aqueous solution was prepared by dissolving cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; sufficient to yield an 18% aqueous solution) in water and heated to a temperature of 80 $^{\circ}\text{C}$. The extrudates were impregnated by immersion in the cobalt nitrate solution for a period of 8 hours at 80 $^{\circ}\text{C}$. The thus impregnated extrudates were dried and finally calcined at a temperature of 500 $^{\circ}\text{C}$ for from 1 to 2 hours.

(ii) Hydrocarbon Synthesis

[0045] The catalyst prepared in (i) hereabove was loaded into a reaction vessel. The catalyst was first activated by reduction by being contacted with a mixture of hydrogen and nitrogen at a temperature of 250 $^{\circ}\text{C}$, a pressure of 5 bar and a gas hourly space velocity of from 500 to 600 NI/hr . The activated catalyst was then contacted with a mixture of carbon monoxide and hydrogen having a hydrogen/carbon monoxide ratio of 1.1 at a gas inlet pressure of from 35 to 40 bars and a gas hourly space velocity of from 1000 to 1200 NI/hr . A heavy wax was produced.

[0046] The effluent of the reaction vessel was collected and the C_4 - components of the mixture removed by distillation. The remaining C_5 + fraction was retained and used directly in the next stage of the process.

(B) FIRST HYDROCONVERSION STAGE

(i) Catalyst Preparation

[0047] A mixture comprising amorphous silica-alumina (ex Grace Davison, pore volume (H_2O) 1.10 ml/g , 13 %wt alumina (dry basis)), and alumina (ex Criterion Catalyst Co.) was placed in a mulling machine and mulled for a period of about 10 minutes. Acetic acid (10 %wt solution) and water were added and the resulting mixture mulled for a further 10 minutes. Thereafter, polyacrylamide ("Superfloc" A1839, 2 %wt aqueous solution) was added and mulling continued for a further 10 minutes. Finally, polyelectrolyte ("Nalco", 4 %wt aqueous solution) was added and the mixture mulled for a final period of about 5 minutes.

[0048] The resulting mixture was extruded using a 5.72 cm (2.25 inch) "Bonnot" extruder through a dieplate, yielding 2.5 mm trilobe extrudates. The resulting extrudates were dried at a temperature of 120 $^{\circ}\text{C}$ for about 2 hours and subsequently calcined at a temperature of 600 $^{\circ}\text{C}$ for 2 hours.

[0049] An aqueous solution was prepared comprising hexachloroplatinic acid (H_2PtCl_6 , 2.45 %wt) and nitric acid (7.66 %wt) having a pH of below 1. The extrudates were impregnated using this aqueous solution via the Pore Impregnation technique to give a final platinum loading on the carrier of 0.8 %wt. The thus impregnated extrudates were finally calcined at a temperature of 500 $^{\circ}\text{C}$ for about 2 hours.

(ii) Hydrocarbon Hydroconversion

[0050] The catalyst prepared in (i) hereabove was loaded into a reaction vessel. The C_5 + hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 0.88 $\text{kg}/\text{l}/\text{hr}$, a temperature of 315 $^{\circ}\text{C}$ and a pressure of 35 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 660 NI/hr (that is a hydrogen to hydrocarbon ratio of 750 NI/kg). Under the aforementioned reaction conditions, the conversion achieved, in terms of percent weight of the fraction of the feed having a boiling point above 370 $^{\circ}\text{C}$ converted

to products having a boiling point of below 370 °C, was 16%, indicating that substantially no cracking or isomerisation of the feed hydrocarbon occurred.

[0051] The effluent of the reaction vessel was collected and the C₄- fraction removed by distillation. The remaining C₅+ fraction was retained and used directly in the next stage.

(C) SECOND HYDROCONVERSION STAGE

(i) Catalyst Preparation

[0052] A catalyst was prepared following the procedure described in Example 1(B)(i) hereabove.

(ii) Hydrocarbon Hydroconversion

[0053] The catalyst prepared in (i) was loaded into a reaction vessel. The C₅+ hydrocarbon product of the first hydroconversion stage was fed to the reaction vessel at a weight hourly space velocity of 1.046 kg/l/hr and a pressure of 31 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 660 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 630 NI/kg). A liquid recycle rate of 0.17 kg/l/hr was applied. A conversion target of 55% (as defined in Example 1(B) (ii) hereabove) was set and was achieved by adjusting the operating temperature of the second hydroconversion stage. It was found that an operating temperature of 330 °C was required.

[0054] The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The properties of a gasoil fraction boiling in the temperature range of from 170 to 340 °C recovered from the effluent are given in Table 1.

EXAMPLE 2

[0055] By way of comparison, product from the hydrocarbon synthesis stage as described in Example 1(A) hereabove was treated to a single hydroconversion stage, operated to yield hydrocarbon fuels.

[0056] A sample of the catalyst prepared as described in Example 1(C)(i) hereabove was loaded into a reaction vessel. The C₅+ hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 1.103 kg/l/hr and a pressure of 31 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 660 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 596 NI/kg). A liquid recycle rate of 0.23 kg/l/hr was applied. A conversion of 55% (as defined in Example 1(B) (ii) hereabove) was achieved at an operating temperature of 338 °C.

[0057] The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The properties of a gasoil fraction boiling in the temperature range of from 170 to 340 °C recovered from the effluent are given in Table 1.

EXAMPLE 3

[0058] As a further comparison, product from the hydrocarbon synthesis stage as described in Example 1(A) hereabove was treated to a single hydroconversion stage, operated to yield hydrocarbon fuels as in Example 2, but operated as follows:

A sample of the catalyst prepared as described in Example 1(C)(i) hereabove was loaded into a reaction vessel. The C₅+ hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 1.01 kg/l/hr and a pressure of 31.4 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 660 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 655 NI/kg). A liquid recycle rate of 0.13 kg/l/hr was applied. A conversion of 39% (as defined in Example 1(B) (ii) hereabove) was achieved at an operating temperature of 334 °C.

[0059] The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The properties of a gasoil fraction boiling in the temperature range of from 160 to 340 °C recovered from the effluent are given in Table 1.

TABLE 1

	Example 1	Example 2	Example 3
Operating Conditions			
Temperature (°C)	330	338	334

TABLE 1 (continued)

	Example 1	Example 2	Example 3
Conversion ¹⁾ %	55	56	39.2
Product Properties			
Cloud Point (°C)	-16	-14.6	-10.1
Pour Point (°C)	-24	-24	-21
CFPP ²⁾ (°C)	-21	-19	-14
Aromatic content ³⁾ (mmole/100g)	0.67	1.51	1.12

1) Defined as percent weight of fraction in feed boiling above 370 °C converted into fraction boiling below 370 °C.

2) Course Filter Plugging Point.

3) Determined using method AMS 392 mod.

EXAMPLE 4

(A) HYDROCARBON SYNTHESIS STAGE

[0060] A catalyst was prepared using the general method outlined in Example 1(A)(i) hereabove and used to prepare a C₅+ hydrocarbon product following the general procedure described in Example 1(A) (ii) hereabove.

(B) FIRST HYDROCONVERSION STAGE

[0061] A commercially available nickel-containing hydrogenation catalyst (60 %wt nickel; ex Harshaw Catalysts) was loaded into a reaction vessel. The C₅+ hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 1.0 kg/l/hr, a temperature of 220 °C and a pressure of 30 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 1000 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 1000 NI/kg). Under the aforementioned reaction conditions, the conversion achieved, in terms of percent weight of the fraction of the feed having a boiling point above 370 °C converted to products having a boiling point of below 370 °C, was less than 5%, indicating that substantially no cracking or isomerisation of the feed hydrocarbon occurred.

[0062] The effluent of the reaction vessel was collected and the C₄-fraction removed by distillation. The remaining C₅+ fraction was retained and used directly in the next stage.

(C) SECOND HYDROCONVERSION STAGE

(i) Catalyst Preparation

[0063] A catalyst was prepared following the procedure described in Example 1(B)(i) hereabove.

(ii) Hydrocarbon Hydroconversion

[0064] The catalyst prepared in (i) was loaded into a reaction vessel. The C₅+ hydrocarbon product of the first hydroconversion stage was fed to the reaction vessel at a weight hourly space velocity of 1.25 kg/l/hr and a pressure of 30 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 1000 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 800 NI/kg). A conversion target of 60% (as defined in Example 4(B) hereabove) was set and achieved by adjusting the operating temperature of the second hydroconversion stage. It was found that an operating temperature of 334 °C was required.

[0065] The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The selectivity of the second hydroconversion stage to a gasoil fraction boiling in the temperature range of from 220 to 370 °C was 50%.

EXAMPLE 5

[0066] By way of comparison, product from the hydrocarbon synthesis stage as described in Example 4(A) hereabove was treated to a single hydroconversion stage, operated to yield hydrocarbon fuels, as follows:

[0067] Catalyst prepared as described in Example 1 (B)(i) was loaded into a reaction vessel. The C₅+ hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 1.25

kg/l/hr and a pressure of 30 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 1000 NV/hr (that is a hydrogen to hydrocarbon ratio of 800 NV/kg). A conversion target of 60% (as defined in Example 4(B) hereabove) was set and achieved by adjusting the operating temperature of the second hydroconversion stage. It was found that an operating temperature of 338 °C was required.

[0068] The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The selectivity of the second hydroconversion stage to a gasoil fraction boiling in the temperature range of from 220 to 370 °C was 40%.

Claims

1. A process for the preparation of gasoil comprising the steps of:

a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic hydrocarbon product, containing at least 70 %wt paraffins;

b) contacting the hydrocarbon product so-obtained with hydrogen in the presence of a hydroconversion catalyst under conditions such that the conversion, defined as the percent weight of the fraction of the hydrocarbon product feed boiling above 370 °C which is converted during the hydroconversion to a fraction boiling below 370°C, is below 20%; separating the C₄- fraction from the higher molecular weight fraction; and

c) contacting at least part of the higher molecular weight hydrocarbon product of step b) with hydrogen in the presence of a hydroconversion catalyst not containing any crystalline zeolite under conditions such that hydrocracking and isomerisation of the hydrocarbon product occurs to yield a substantially paraffinic hydrocarbon fuel, containing at least 95 %wt paraffins, and isolating the gasoil from the hydrocarbon fuel, the conversion being at least 40 %.

2. A process according to claim 1, **characterised in that** the mixture of carbon monoxide and hydrogen contacting the catalyst in step (a) has a hydrogen/carbon monoxide ration of less than 2.5, preferably less than 1.75, more preferably of from 0.4 to 1.5.

3. A process according to either of claims 1 or 2, **characterised in that** the hydrocarbon synthesis catalyst in step (a) comprises ruthenium, iron, nickel or cobalt as a catalytically active metal, preferably cobalt.

4. A process according to any preceding claim, **characterised in that** the hydrocarbon synthesis catalyst in step (a) comprises a carrier, preferably selected from silica, alumina, titania, zirconia, and mixtures thereof, most preferably silica or alumina.

5. A process according to any preceding claim, **characterised in that** the hydrocarbon synthesis catalyst in step (a) comprises as a promoter an oxide of a metal selected from Group IVB of the Periodic Table of Elements, preferably titanium or zirconium.

6. A process according to any preceding claim, **characterised in that** the mixture of carbon monoxide and hydrogen is contacted with the catalyst in step (a) at a temperature of from 125 to 300 °C, preferably from 175 to 250 °C.

7. A process according to any preceding claim, **characterised in that** the mixture of carbon monoxide and hydrogen is contacted with the catalyst in step (a) at a pressure of from 5 to 100 bars, preferably from 12 to 50 bars.

8. A process according to any preceding claim, **characterised in that** the hydroconversion catalyst of step (b) comprises molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum or palladium as a catalytically active metal, preferably one or more of nickel, platinum and palladium.

9. A process according to any preceding claim, **characterised in that** the hydroconversion catalyst of step (b) comprises a carrier, preferably selected from silica, alumina, silica-alumina, titania, zirconia and mixtures thereof, preferably silica, alumina or silica-alumina.

10. A process according to any preceding claim, **characterised in that** in step (b) the hydrocarbon product is contacted with the hydroconversion catalyst at a temperature of from 100 to 300 °C, preferably from 150 to 275 °C.

11. A process according to any preceding claim, **characterised in that** in step (b) the hydrocarbon product is contacted with the hydroconversion catalyst at a pressure of from 5 to 150 bars, preferably from 10 to 50 bars.
12. A process according to any preceding claim, **characterised in that** in step (b) hydrogen is provided at a gas hourly space velocity of from 100 to 10000 NI/hr preferably from 250 to 5000 NI/hr.
13. A process according to any preceding claim, **characterised in that** in step (b) the conversion is below 10%, more preferably below 5%.
14. A process according to any preceding claim, **characterised in that** the hydroconversion catalyst of step (c) comprises molybdenum, tungsten, cobalt; nickel, ruthenium, iridium, osmium, platinum or palladium as a catalytically active metal, preferably one or more of nickel, platinum and palladium.
15. A process according to any preceding claim, **characterised in that** the hydroconversion catalyst of step (c) comprises a carrier, preferably selected from silica, alumina, silica-alumina, titania; zirconia and mixtures thereof, preferably silica, alumina or silica-alumina.
16. A process according to any preceding claim, **characterised in that** in step (c) the hydrocarbon product is contacted with the hydroconversion catalyst at a temperature of from 175 to 400 °C, preferably from 250 to 375 °C.
17. A process according to any preceding claim, **characterised in that** in step (c) the hydrocarbon product is contacted with the hydroconversion catalyst at a pressure of from 10 to 250 bars, preferably from 25 to 250 bars.
18. A process according to any preceding claim, **characterised in that** in step (c) hydrogen is provided at a gas hourly space velocity of from 100 to 10000 NI/hr, preferably from 500 to 5000 NI/hr.
19. A process according to any preceding claim, **characterised in that** the light components, preferably the C₄- components, are removed from the product of the hydrocarbon synthesis of step (a).

Patentansprüche

1. Verfahren zur Herstellung von Gasöl, welches die folgenden Stufen umfaßt:
 - a) Inberührungbringen eines Gemisches aus Kohlenmonoxid und Wasserstoff mit einem Kohlenwasserstoffsynthesekatalysator bei erhöhter Temperatur und erhöhtem Druck zur Ausbildung eines im wesentlichen paraffinischen Kohlenwasserstoffproduktes, das wenigstens 70 Gew.-% Paraffine enthält;
 - b) Inberührungbringen des so erhaltenen Kohlenwasserstoffproduktes mit Wasserstoff in Anwesenheit eines Hydrokonversionskatalysators unter solchen Bedingungen, daß die Umwandlung, definiert als Gewichtsprozent der Fraktion der Kohlenwasserstoffprodukteinspeisung, die über 370°C siedet, welche während der Hydrokonversion zu einer unter 370°C siedenden Fraktion umgewandelt wird, unter 20% liegt; Abtrennen der C₄-Fraktion von der Fraktion mit höherem Molekulargewicht; und
 - c) Inberührungbringen wenigstens eines Teiles des Kohlenwasserstoffproduktes mit höherem Molekulargewicht aus Stufe b) mit Wasserstoff in Anwesenheit eines Hydrokonversionskatalysators, der keinerlei kristallinen Zeolith enthält, unter solchen Bedingungen, daß ein Hydrocracken und Isomerisieren des Produktes eintritt, um einen im wesentlichen paraffinischen Kohlenwasserstoffbrennstoff zu ergeben, der wenigstens 95 Gew.-% Paraffine enthält, und Isolieren des Gasöls aus dem Kohlenwasserstoffbrennstoff, wobei die Umwandlung wenigstens 40% beträgt.
2. Verfahren nach Anspruch 1 **dadurch gekennzeichnet, daß** das mit dem Katalysator in Stufe (a) in Berührung kommende Gemisch aus Kohlenmonoxid und Wasserstoff ein Wasserstoff/Kohlenmonoxid-Verhältnis von kleiner als 2,5, vorzugsweise kleiner als 1,75, stärker bevorzugt von 0,4 bis 1,5 aufweist.
3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** der Kohlenwasserstoffsynthesekatalysator in Stufe (a) als katalytisch aktives Metall Ruthenium, Eisen, Nickel oder Kobalt, vorzugsweise Kobalt enthält.
4. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der Kohlenwasserstoffsynthesekatalysator in Stufe (a) einen Träger umfaßt, vorzugsweise ausgewählt unter Siliziumdioxid, Aluminiumoxid,

Titanoxid, Zirkonoxid und Gemischen hievon, am meisten bevorzugt Siliziumdioxid oder Aluminiumoxid.

5. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der Kohlenwasserstoffsynthesekatalysator in Stufe (a) als Promotor ein Oxid eines aus der Gruppe IVB des Periodensystems der Elemente ausgewählten Metalles, vorzugsweise Titan oder Zirkon, enthält.
6. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** das Gemisch aus Kohlenmonoxid und Wasserstoff mit dem Katalysator in Stufe (a) bei einer Temperatur von 125 bis 300 °C, vorzugsweise von 175 bis 250°C in Kontakt gebracht wird.
7. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** das Gemisch aus Kohlenmonoxid und Kohlenwasserstoff mit dem Katalysator in Stufe (a) bei einem Druck von 5 bis 100 bar, vorzugsweise von 12 bis 50 bar in Kontakt gebracht wird.
8. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der Hydrokonversionskatalysator von Stufe (b) als katalytisch aktives Metall Molybdän, Wolfram, Kobalt, Nickel, Ruthenium, Iridium, Osmium, Platin oder Palladium enthält, vorzugsweise eines oder mehrere von Nickel, Platin und Palladium.
9. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der Hydrokonversionskatalysator von Stufe (b) einen Träger enthält, vorzugsweise ausgewählt unter Siliziumdioxid, Aluminiumoxid, Siliziumdioxid-Aluminiumoxid, Titanoxid, Zirkonoxid und Gemischen hievon, vorzugsweise Siliziumdioxid, Aluminiumoxid oder Siliziumdioxid-Aluminiumoxid.
10. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** in Stufe (b) das Kohlenwasserstoffprodukt bei einer Temperatur von 100 bis 300°C, vorzugsweise von 150 bis 275°C mit dem Hydrokonversionskatalysator in Kontakt gebracht wird.
11. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** in Stufe (b) das Kohlenwasserstoffprodukt bei einem Druck von 5 bis 150 bar, vorzugsweise 10 bis 50 bar mit dem Hydrokonversionskatalysator in Kontakt gebracht wird.
12. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** in Stufe (b) der Wasserstoff mit einer Gas-Raumgeschwindigkeit von 100 bis 10.000 NI/h, vorzugsweise von 250 bis 5.000 NI/h zugeführt wird.
13. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** in Stufe (b) die Umwandlung unter 10%, stärker bevorzugt unter 5% gehalten wird.
14. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der Hydrokonversionskatalysator von Stufe (c) als katalytisch aktives Metall Molybdän, Wolfram, Kobalt, Nickel, Ruthenium, Iridium, Osmium, Platin oder Palladium enthält, vorzugsweise eines oder mehrere von Nickel, Platin und Palladium.
15. Verfahren nach einem der vorstehenden Ansprüche **dadurch gekennzeichnet, daß** der Hydrokonversionskatalysator von Stufe (c) einen Träger umfaßt, vorzugsweise ausgewählt unter Siliziumdioxid, Aluminiumoxid, Siliziumdioxid-Aluminiumoxid, Titanoxid, Zirkonoxid und Gemischen hievon, vorzugsweise Siliziumdioxid, Aluminiumoxid oder Siliziumdioxid-Aluminiumoxid.
16. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** in Stufe (c) das Kohlenwasserstoffprodukt bei einer Temperatur von 175 bis 400°C, vorzugsweise von 250 bis 375°C mit dem Hydrokonversionskatalysator in Kontakt gebracht wird.
17. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** in Stufe (c) das Kohlenwasserstoffprodukt bei einem Druck von 10 bis 250 bar, vorzugsweise von 25 bis 250 bar mit dem Hydrokonversionskatalysator in Kontakt gebracht wird.
18. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** in Stufe (c) der Wasserstoff mit einer Raumgeschwindigkeit von 100 bis 10.000 NI/h, vorzugsweise von 500 bis 5.000 NI/h zugeführt wird.

19. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** die leichten Komponenten, vorzugsweise die C₄-Komponenten, aus dem Produkt aus der Kohlenwasserstoffsynthesestufe (a) abgetrennt werden.

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Revendications

1. Procédé de préparation de carburants hydrocarbonés, **caractérisé en ce qu'il** comprend les étapes consistant à :
 - a) mettre en contact un mélange de monoxyde de carbone et d'hydrogène avec un catalyseur de synthèse d'hydrocarbures, à température et pression élevées, de manière à préparer un produit hydrocarboné sensiblement paraffinique, contenant au moins 70% en poids de paraffines;
 - b) mettre en contact le produit hydrocarboné ainsi obtenu avec de l'hydrogène en présence d'un catalyseur d'hydroconversion dans des conditions telles que la conversion, définie comme le pourcentage pondéral de la fraction de la charge de produit hydrocarboné bouillant au-delà de 370°C et qui est convertie au cours de l'hydroconversion en une fraction bouillant en dessous de 370°C, demeure inférieure à 20%; séparer la fraction en C₄- de la fraction de poids moléculaire supérieur; et
 - c) mettre en contact au moins une partie du produit hydrocarboné de poids moléculaire supérieur de l'étape (b) avec de l'hydrogène en présence d'un catalyseur d'hydroconversion ne contenant pas de zéolite cristalline, dans des conditions telles que l'hydrocraquage et l'isomérisation du produit s'opèrent pour donner un carburant hydrocarboné sensiblement paraffinique, contenant au moins 95% en poids de paraffines, et isoler le gazole du carburant hydrocarboné, la conversion étant d'au moins 40%.
2. Procédé suivant la revendication 1, **caractérisé en ce que** le mélange de monoxyde de carbone et d'hydrogène entrant en contact avec le catalyseur dans l'étape (a) possède un rapport hydrogène/monoxyde de carbone inférieur à 2,5, de préférence, inférieur à 1,75, plus avantageusement, de 0,4 à 1,5.
3. Procédé suivant l'une quelconque des revendications 1 ou 2, **caractérisé en ce que** le catalyseur de synthèse d'hydrocarbures de l'étape (a) comprend du ruthénium, du fer, du nickel, ou du cobalt, à titre de métal catalytiquement actif, de préférence, du cobalt.
4. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** le catalyseur de synthèse d'hydrocarbures dans l'étape (a) comprend un support, de préférence, choisi parmi la silice, l'alumine, l'oxyde de titane, la zircone et leurs mélanges, plus avantageusement, la silice ou l'alumine.
5. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** le catalyseur de synthèse d'hydrocarbures dans l'étape (a) comprend, à titre de promoteur, un oxyde d'un métal choisi parmi les éléments du groupe IVB du tableau périodique, de préférence, le titane ou le zirconium.
6. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** l'on met le mélange de monoxyde de carbone et d'hydrogène en contact avec le catalyseur dans l'étape (a), à une température qui varie de 125 à 300°C, de préférence, de 175 à 250°C.
7. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** l'on met le mélange de monoxyde de carbone et d'hydrogène en contact avec le catalyseur dans l'étape (a), sous une pression de 5 à 100 bars, de préférence, de 12 à 50 bars.
8. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** le catalyseur d'hydroconversion de l'étape (b) comprend du molybdène, du tungstène, du cobalt, du nickel, du ruthénium, de l'iridium, de l'osmium, du platine ou du palladium, à titre de métal catalytiquement actif, de préférence, un ou plusieurs éléments choisis parmi le nickel, le platine et le palladium.
9. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** le catalyseur d'hydroconversion de l'étape (b) comprend un support, de préférence, choisi parmi la silice, l'alumine, la silice-alumine, l'oxyde de titane, la zircone et leurs mélanges, plus avantageusement, la silice, l'alumine et la silice-alumine.
10. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** dans l'étape (b), on met le produit hydrocarboné en contact avec le catalyseur d'hydroconversion, à une température qui varie de 100

à 300°C, de préférence, de 150 à 275°C.

- 5 11. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** dans l'étape (b), on met le produit hydrocarboné en contact avec le catalyseur d'hydroconversion, sous une pression de 5 à 150 bars, de préférence, de 10 à 50 bars.
- 10 12. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** dans l'étape (b), on fournit l'hydrogène à la vitesse spatiale horaire gazeuse de 100 à 1000 litres normaux/litre/ heure, de préférence, 250 à 5000 litres normaux/litre/heure.
- 15 13. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** dans l'étape (b), la conversion est inférieure à 10%, plus avantageusement encore, inférieure à 5%.
- 20 14. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** le catalyseur d'hydro-conversion de l'étape (c) comprend du molybdène, du tungstène, du cobalt, du nickel, du ruthénium, de l'iridium, de l'osmium, du platine ou du palladium, à titre de métal catalytiquement actif, de préférence un ou plusieurs éléments choisis parmi le nickel, le platine et le palladium.
- 25 15. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** le catalyseur d'hydro-conversion de l'étape (c) comprend un support, choisi, de préférence, parmi la silice, l'alumine, la silice-alumine, l'oxyde de titane, la zircone et leurs mélanges, de préférence, la silice, l'alumine et la silice-alumine.
- 30 16. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** dans l'étape (c), on met le produit hydrocarboné en contact avec le catalyseur d'hydroconversion, à une température qui varie de 175 à 400°C, de préférence, de 250 à 375°C.
- 35 17. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** dans l'étape (c), on met le produit hydrocarboné en contact avec le catalyseur d'hydroconversion, sous une pression de 10 à 250 bars, de préférence, de 25 à 250 bars.
- 40 18. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** dans l'étape (c), on fournit l'hydrogène à une vitesse spatiale horaire gazeuse de 100 à 10000 litres normaux/litre/ heure, de préférence, de 500 à 5000 litres normaux/litre/heure.
- 45 19. Procédé suivant l'une quelconque des revendications précédentes, **caractérisé en ce que** l'on élimine les composants légers, de préférence, les composants en C₄, du produit de la synthèse d'hydrocarbures de l'étape (a).
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